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Quantifying natural source mercury emissions from the Ivanhoe Mining District, north-central Nevada, USA

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Abstract

In order to assess the importance of mercury emissions from naturally enriched sources relative to anthropogenic point sources, data must be collected that characterizes mercury emissions from representative areas and quantifies the influence of various environmental parameters that control emissions. With this information, we will be able to scale up natural source emissions to regional areas. In this study in situ mercury emission measurements were used, along with data from laboratory studies and statistical analysis, to scale up mercury emissions for the naturally enriched Ivanhoe Mining District, Nevada. Results from stepwise multi-variate regression analysis indicated that lithology, soil mercury concentration, and distance from the nearest fault were the most important factors controlling mercury flux. Field and lab experiments demonstrated that light and precipitation enhanced mercury emissions from alluvium with background mercury concentrations. Diel mercury emissions followed a Gaussian distribution. The Gaussian distribution was used to calculate an average daily emission for each lithologic unit, which were then used to calculate an average flux for the entire area of $17.1 \text{ ng Hg m}^{-2} \text{ h}^{-1}$. An annual emission of $\sim 8.7 \times 10^4 \text{ g}$ of mercury to the atmosphere was calculated for the 586 km^2 area. The bulk of the Hg released into the atmosphere from the district ($\sim 89\%$) is from naturally enriched non-point sources and $\sim 11\%$ is emitted from areas of anthropogenic disturbance where mercury was mined. Mercury emissions from this area exceed the natural emission factor applied to mercury rich belts of the world ($1.5 \text{ ng m}^{-2} \text{ h}^{-1}$) by an order of magnitude. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Mercury; Atmospheric mercury; Mercury emission; Natural sources; Atmosphere-surface exchange

1. Introduction

1.1. Purpose and scope of paper

The magnitude of mercury (Hg) emissions from naturally enriched substrate relative to anthropogenic point sources into the atmosphere is disputed (Gustin et al., 1999a; Lindqvist et al., 1991). Current biogeochemical cycles apply an average emission factor of

$\sim 1.5 \text{ ng Hg m}^{-2} \text{ h}^{-1}$ to naturally enriched areas (Lindqvist et al., 1991; Mason et al., 1994). At the time of the development of these models there were no published studies that quantified Hg emission from naturally enriched areas. Recent studies have begun to focus on the measurement of Hg flux from naturally Hg enriched areas (Gustin et al., 1999a, 2000b; Rasmussen et al., 1998). In 1997, researchers involved with the measurement of Hg flux from terrestrial and aquatic landscapes gathered at the naturally enriched Steamboat Springs Geothermal Area, Nevada, USA to measure Hg fluxes occurring at the site ($\sim 100 \text{ ng m}^{-2} \text{ h}^{-1}$) (Gustin et al., 1999a). This project demonstrated to the Hg research community that naturally enriched substrate could be a significant source of Hg to the atmosphere.

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In order to adequately quantify the emission of Hg from naturally enriched areas, Hg flux must be determined for a variety of enriched and mineralized areas. Naturally Hg-enriched substrate is found associated with plate tectonic boundaries; areas of high crustal heat flow; precious and base metal mineralization; Hg mineralization; recent volcanism; and organic rich sedimentary rocks (Rasmussen, 1994). Large areas of land in the western United States are enriched in Hg and Hg deposits are abundant (Jonasson and Boyle, 1972). Mercury in soil gas and the atmosphere has been used as a tool in exploration for geothermal reservoirs, ore deposits, and geologic structures (McCarthy and McGuire, 1998; McCarthy, 1972).

Without a clear understanding of the magnitude of emissions from natural sources the global biogeochemical cycle for Hg is not complete. Currently, through the use of the Toxic Release Inventory, emissions of Hg from anthropogenic sources such as coal-fired power plants, metal refineries, and incinerators are being made publicly available. In December 2000, the EPA announced its intention to regulate Hg emissions from fossil fuel electric power plants under the Clean Air Act (Environmental Reporter, 2000). The relative magnitude of emissions from natural non-point sources relative to point sources

must be assessed in order to determine whether controls on anthropogenic point sources will be effective.

The purpose of this study was to develop a Hg emission estimate for a naturally enriched area, the Ivanhoe Mining District, Elko County, Nevada (Fig. 1). In order to do this those variables most influential in controlling Hg flux had to be determined. Micrometeorological and geological parameters, measured in the field simultaneously with Hg flux measurements, were examined using regression analysis to determine those parameters most strongly influencing Hg flux. Understanding those parameters dominant in controlling flux will allow for estimation of Hg flux from other similar areas where flux measurements were not made and areas where access is limited. Laboratory flux experiments were applied to examine the influence of light, air Hg concentration, and precipitation on Hg flux. A Geographic Information System (GIS) was used to assimilate environmental variables and flux data to determine the total Hg flux from the study area.

1.2. Study site

The Ivanhoe Mining District is located in north-central Nevada at the northern extent of the

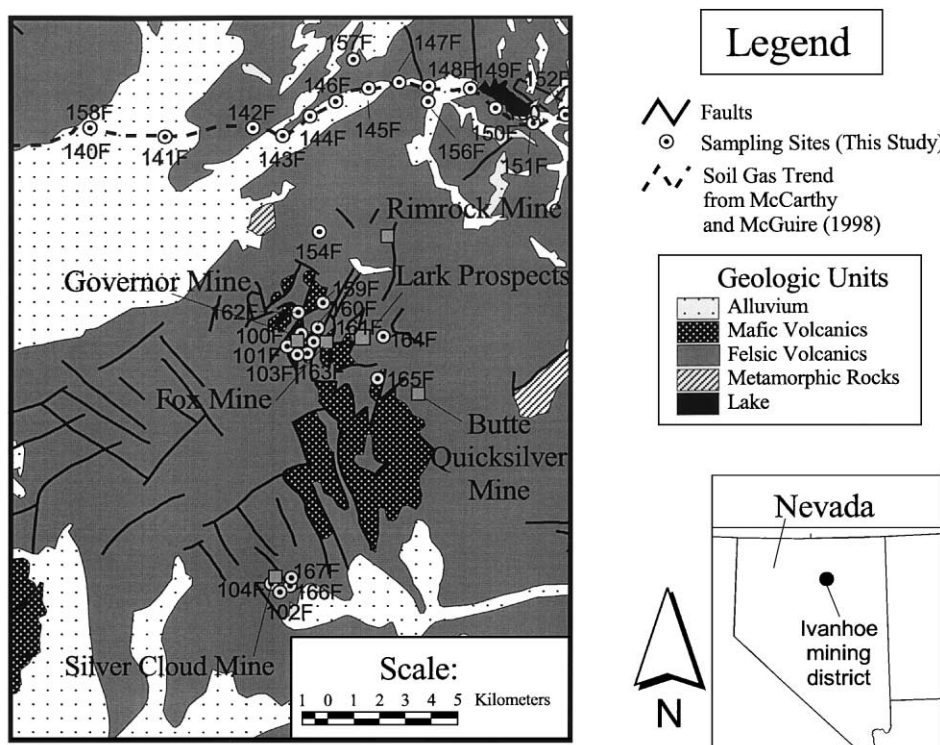


Fig. 1. Geologic map of the Ivanhoe Mining District and surrounding area. Dashed line indicates soil gas sampling transect used by McCarthy and McGuire (1998). Sampling locations are noted by bulls-eye symbol. Locations of abandoned Hg mines are noted by gray squares. Samples were taken in areas of both Hg mineralization and in distal, less Hg enriched areas.

World-Class gold-bearing Carlin Trend (Fig. 1). Approximately 13 open pit gold mines are located along the Carlin Trend, where Hg is a common geochemical byproduct of the gold extraction process (Rytuba and Heropoulos, 1992). The Ivanhoe Mining District consists of Eocene to Miocene felsic and mafic volcanic rocks that mantle Paleozoic sedimentary rocks (argillite and chert) of the Carlin Trend (Wallace, 1991). Active hydrothermal systems during the mid-Miocene produced Hg enrichment and mineralization throughout the district. Mercury deposits, formed adjacent to faults within the felsic tuffs and tuffaceous sediments, contain cinnabar (HgS), calomel (Hg₂Cl₂), and quicksilver (Hg) (Bailey and Phoenix, 1944).

Meteorological data collected within the district (Newmont Gold Company, 1997) show that the Ivanhoe Mining District is fairly typical of a high desert environment. Average monthly temperatures range from at or below freezing (generally -5 to 1°C) in December and January to the upper 10s and lower 20s in July and August. Precipitation values generally range from 20 to 30 cm annually, with the majority of the precipitation occurring during December, January, March, April and May and with little or no precipitation during July and August. Meteoric conditions during the fall and spring are generally representative of average yearly conditions within the district.

1.3. Previous work

Pierce et al. (1970) characterized Hg in rocks and soils from the Ivanhoe Mining District and reported that $>50\%$ of the 519 rock samples from the Ivanhoe Mining District exceeded $25\mu\text{g g}^{-1}$ and 50% of the 681 soil samples collected exceeded $0.20\mu\text{g g}^{-1}$ Hg. Given that substrate is considered naturally enriched in Hg when concentrations are $>0.1\mu\text{g g}^{-1}$ (Gustin et al., 2000b), the substrate of the Ivanhoe District is significantly enriched relative to natural background concentrations.

Almost 90% of the Hg from the Ivanhoe Mining District was produced from the Butte Quicksilver ($\sim 36,000$ kg recovered) and Silver Cloud ($\sim 30,000$ kg recovered) mines from 1915 to 1943 (Fig. 1) (Bailey and Phoenix, 1944). Several other small Hg mines, including the Fox and Governor mines, in the district produced in total $\sim 10,000$ kg of Hg.

McCarthy and McGuire (1998) sampled H₂, O₂, CO₂, and hydrocarbon gases on an east-west trend along the north end of the district (Fig. 1). They found elevated H₂ and CO₂ levels in the soil gas along structures potentially related to the Carlin Trend. Mercury flux was measured along the same transect as McCarthy and McGuire (1998) in this study to discern whether there was a relationship between Hg flux and anomalous soil gas concentrations.

2. Methods

2.1. Soil Hg flux and micrometeorological data collection

In order to determine the distribution and magnitude of Hg flux from soils within the Ivanhoe Mining District, in situ flux chamber measurements were taken at 31 sites throughout the district from representative geologic units and types of hydrothermal alteration (Fig. 1). Three types of field chambers were used in this study, Oak Ridge National Laboratory's (ORNL) Teflon[®] flux chamber (Gustin et al., 1999a), ORNL's polycarbonate flux chamber and the University of Nevada, Reno's (UNR) polycarbonate flux chamber. The ORNL Teflon[®] flux chamber was used to measure diel Hg flux, just south of the district in the fall of 1998. The ORNL Teflon[®] flux chamber is a rectangular Teflon[®] box ($20 \times 20 \times 60\text{ cm}^3$) with a 24 l volume and a 1.0 min turnover rate. The ORNL polycarbonate chamber was used to measure Hg emissions at four sampling sites within the Ivanhoe Mining District, also during the fall of 1998. This polycarbonate chamber has a volume of 11.2 l and a turnover rate of 0.45 min. An intercomparison of fluxes measured at the Ivanhoe Mining District with the ORNL polycarbonate chamber and the ORNL Teflon[®] chamber showed good agreement (mean ORNL polycarbonate chamber flux = $35\text{ ng m}^{-2}\text{ h}^{-1}$, mean ORNL Teflon[®] chamber flux = $28.9\text{ ng m}^{-2}\text{ h}^{-1}$). At the rest of the field sites, visited in the fall of 1999, the UNR flux chamber was used. The UNR chamber consists of a cylindrical polycarbonate chamber with a radius of 10 cm, a height of 3.5 cm, a 1 l volume, and a 0.10 min turnover rate. Sixteen holes (1 cm diameter) were drilled around the circumference of the polycarbonate flux chamber allowing unrestricted airflow. This high chamber turnover rate was applied based on studies that have shown that low chamber turnover rates can suppress Hg flux (Gustin et al., 1999a; Wallschläger et al., 1999). Experiments and theoretical modeling recently done by author Zhang and colleagues have demonstrated that the turnover rate used with the UNR field chamber is optimal for the measurement of flux. In this paper we have used the fluxes measured and have not applied any correction factors to adjust for the fact that the turnover times applied in 1998 by the ORNL chambers is less than optimal. The lower turnover rate will suppress emissions and therefore 1998 fluxes reported are conservative.

Two methods were used to quantify Hg. For the ORNL Teflon[®] flux chamber and the UNR polycarbonate flux chamber, the inlet and outlet air streams were sampled by a Tekran[®] (Model 2537A) CVAFS. The Tekran[®] measures Hg concentration of the air in 5 min intervals allowing for assessment of almost real time flux and of the influence of environmental parameters on Hg

Table 1

Mercury flux values measured for specific lithologic units in the Ivanhoe Mining District

Location	Ambient Hg conc. at the inlet (ng m ⁻³)	Measured Hg flux (ng m ⁻² hr ⁻¹)	Calculated average hourly flux (ng m ⁻² hr ⁻¹)	Hg substrate concentration bulk sample (ng g ⁻¹)	Lithologic unit
100F	40.5 ± 5.6	652	280	67,600	Governor mine site
101F	10.7 ± 0.7	101	38.9	11,800	Mine waste
102F	10.7 ± 0.4	564	226	30,500	Mine waste
103F	5.8 ± 13	6.2	2.63	483	Felsic volcanic rocks
104F	1703 ± 774	59,100	27,600	9,060,000	Silver cloud mine site
140F	5.47 ± 1.73	-51.7	0	95	Alluvium
141F	1.45 ± 0.13	-0.1	0	45	Alluvium
142F	2.37 ± 0.21	4.5	2.43	101	Felsic volcanic rocks
143F	4.02 ± 0.22	109	44.8	330	Felsic volcanic rocks
144F	3.23 ± 0.12	-13.3	0	23	Alluvium
145F	2.39 ± 0.32	-13.9	0	21	Alluvium
146F	2.26 ± 0.13	-17.6	0	27	Alluvium
147F	2.24 ± 0.33	-19.9	0	22	Alluvium
148F	2.60 ± 0.27	-11.2	0	43	Alluvium
149F	9.15 ± 0.80	-23.6	0	32	Alluvium
150F	3.33 ± 0.34	-14.5	0	55	Alluvium
151F	2.66 ± 0.28	-19.4	0	32	Alluvium
152F	2.35 ± 0.37	-15	0	19	Alluvium
154F	1.20 ± 0.20	29.8	12.3	1940	Felsic volcanic rocks
156F	7.80 ± 0.75	28.6	17.7	70	Felsic volcanic rocks
157F	1.96 ± 1.30	29.7	13.3	24	Felsic volcanic rocks
158F	1.53 ± 0.13	-4.4	0	114	Alluvium
159F	5.07 ± 0.49	-61.9	0	1060	Mafic volcanic rocks
160F	1.82 ± 0.34	0	0	2390	Felsic volcanic rocks
161F	2.13 ± 0.53	33.8	28.1	5080	Felsic volcanic rocks
162F	2.25 ± 0.88	42.4	25.7	5610	Felsic volcanic rocks
163F	2.42 ± 0.31	8.8	4.00	1410	Mafic volcanic rocks
164F	2.34 ± 0.52	35.9	13.9	125	Felsic volcanic rocks
165F	4.10 ± 0.77	41.9	16.8	5060	Mafic volcanic rocks
166F	5.16 ± 1.26	103.7	53.9	9720	Felsic volcanic rocks
167F	2.49 ± 0.97	34.9	25.2	2360	Felsic volcanic rocks

flux (Gustin et al., 1999a). A Tekran[®] Automated Dual Sampling (TADS) unit was used to sequentially sample the air at the inlet and outlet of the chamber in 10 min intervals (two samples). Hg flux was calculated using the following equation:

$$F = Q(C_o - C_i)/A,$$

where F is the total flux in ng Hg m⁻² h⁻¹; C_o and C_i are the Hg concentration measured at the outlet and inlet in ng Hg m⁻³; A is the surface area exposed in the flux chamber in m²; and Q is the flow of ambient air through the flux chamber in m³ h⁻¹. Mercury concentrations at the inlet (C_i) of the chamber are reported in Table 1 as “ambient” concentrations. The inlet concentrations will overestimate ambient air Hg concentrations in areas where Hg is being emitted from substrate. This is because Hg concentrations decrease exponentially away from the ground surface, due to dilution (Gustin et al., 1996), and the inlet is located only 2–3 cm from the

ground surface. Mercury concentrations were measured at each location for at least 40 min, or until Hg flux values had stabilized. Chamber blanks during the study were measured during the study by placing a clean polycarbonate plate under the flux chamber and averaged 2.5 ± 1.3 ng m⁻² h⁻¹ ($n = 7$).

For the ORNL polycarbonate flux chamber, Hg in air was collected on triplicate in parallel gold-coated quartz sand traps at the inlet and outlet of the flux chamber at a rate of 0.51 min⁻¹, controlled using Tylan General high precision mass flow controllers. The gold quartz traps were taken back to lab and analyzed for total Hg using a Cold Vapor Atomic Fluorescence Spectrometer (CVAFS) (Bloom and Fitzgerald, 1988). The results for total Hg from the gold-coated quartz sand traps were divided by the volume of air sampled to determine C_o and C_i . The total flux was calculated as described above.

At each sampling location micrometeorological data including air and soil temperature (Omega

thermocouple), relative humidity (Vaisala CS500), barometric pressure (Vaisala CS105), and light intensity (Li-Cor LI200X) were collected on 5 min intervals using a Campbell CR21X data logger for the 1999 data. Substrate samples (1–2 cm depth) were collected from each of the flux chamber sampling sites after the flux measurements had been performed. The samples were pulverized, then analyzed for total Hg, after aqua regia digestion, using Atomic Absorption Spectrometry by the Nevada Bureau of Mines and Geology (Lechler, 1999).

2.2. Laboratory Hg flux experiments

Laboratory-based Hg flux chamber experiments have shown good agreement with field measurements (Gustin et al., 1999b). Laboratory studies allow for investigation of the factors influencing Hg emission in a controlled setting. In the field, many environmental and substrate factors influence Hg flux, confounding the assessment of the effect of individual variables.

Samples of alluvium collected from the transect of McCarthy and McGuire (1998) were used for laboratory studies. These soils were coarse, sand dominated (50–60% by weight), and commonly contained platy and vesicular horizons, indicating a high clay content (15–30% by weight). The organic carbon content of these soils, determined using a Perkin Elmer 2400 CHNS analyzer, was low ($1.22 \pm 0.74\%$, $n = 11$).

To examine the potential for Hg uptake and release by alluvium, samples were exposed to different air Hg concentrations using the same UNR flux chamber and sampling methods applied in the field and a 1 cm layer of soil within a PlexiglasTM box. The same soil sample was used throughout the series of experiments and the range in time between individual experiments ranged from six hours to one day. The concentration of Hg entering the PlexiglasTM box was controlled at 0 ng m^{-3} , ambient ($3.9 \pm 2.2 \text{ ng m}^{-3}$), 20 ng m^{-3} , and 220 ng m^{-3} . Ambient greenhouse air concentrations ($3.9 \pm 2.2 \text{ ng m}^{-3}$) were on the same order of magnitude as ambient air Hg concentrations in the field (Table 1). The 0, 20, and 220 ng m^{-3} air was cleaned air generated using an Aadco pure air generator (model 737R-10). To introduce Hg into the cleaned air for the 20 and 220 ng m^{-3} air, Hg was permeated using a Kin-Tec Precision Gas Standards Generator System and a Hg permeation tube (VICI Metronics) into the pure air stream. The effect of precipitation and light on Hg uptake and release by alluvium soils were investigated by spraying soil in the chamber with 10 and 30 ml aliquots of nanopure water (filtered with a Milli-Q[®] Millipore system) and through controlled light experiments. Nanopure water was used because its low Hg concentration ($\leq 0.02 \text{ ng l}^{-1}$) could not introduce appreciable Hg into the chamber.

2.3. Data analysis

To determine the relative importance of specific environmental parameters on Hg soil flux, micrometeorological data, distance to the nearest fault, lithology, and total Hg concentrations of soils were correlated with Hg flux using stepwise multivariate regression analysis with the program StatView[®]. Natural logarithm values of soil Hg concentration and distance from sample location to the nearest fault were used due to their lognormal distributions. The regression coefficient (R^2) of each variable was compared to rank the data from most to least important/predictive. The Fisher F-value was used to calculate the significance of the independent variables on Hg flux.

Geologic units and faults were input into a Geographic Information System (GIS) (Coats, 1987). Lithologic units were grouped into four main categories: alluvium, felsic volcanic rocks, mafic volcanic rocks, and metamorphic rocks, and the area of each unit was calculated within the GIS.

3. Results and discussion

3.1. In situ soil Hg flux

Mercury fluxes were the greatest in areas where Hg was mined (Table 1). In situ Hg fluxes measured from felsic volcanic rocks outside of mined and disturbed areas ranged from 4.5 to $109 \text{ ng m}^{-2} \text{ h}^{-1}$. Mafic volcanic rocks exhibited lower flux values ranging from -61.9 to $41.9 \text{ ng m}^{-2} \text{ h}^{-1}$. Fluxes from alluvium were negative (-51.7 to $-0.1 \text{ ng m}^{-2} \text{ h}^{-1}$). Chamber blanks, taken in the field to ensure that the negative measurements were not a result of contamination or analytical error, yielded slightly positive values ($2.5 \pm 1.3 \text{ ng m}^{-2} \text{ h}^{-1}$, $n = 7$). Mercury fluxes presented in Table 1 are not corrected for the mean chamber blank. However, sample location 160F had a positive measured Hg flux ($2.1 \text{ ng m}^{-2} \text{ h}^{-1}$) that was lower than the flux measured in chamber blanks. Therefore, the Hg flux from this site was assumed to be $0 \text{ ng m}^{-2} \text{ h}^{-1}$, as shown in Table 1.

Negative Hg flux values are measured with the field chamber when the inlet Hg concentration is greater than the outlet concentration of the flux chamber. This would be expected if the inlet was placed over a small area with much higher Hg flux than any area in the flux chamber. This mechanism is highly unlikely given the design of the flux chamber. Negative Hg flux values could also be a result of Hg sorption in the field chamber, but chamber blanks yielded slightly positive values ($2.5 \pm 1.3 \text{ ng m}^{-2} \text{ h}^{-1}$), indicating that if anything, the flux chamber is a weak source of Hg, not a Hg sink. Advection of Hg from a nearby source is an unlikely candidate to produce a negative Hg flux because the Hg

would be equally detected in both at the inlet and outlet of the flux chamber. Mercury emissions would also be negative if the soils under the chamber were actively sorbing gaseous Hg within the flux chamber. The sorption of elemental Hg vapor by soils has been observed in laboratory experiments and a correlation was observed for Hg uptake, organic matter, and clay mineral content in the soil (Fang, 1978; Farrah and Pickering, 1978).

The interaction of light and water with soils has been demonstrated to rapidly pulse Hg from substrate (Gustin et al., 1999a, 1998; Lindberg et al., 1999). The addition of water has been shown to increase Hg flux in desert soils and is hypothesized to be due to exchange of water molecules with elemental Hg and/or Hg^{2+} , Hg_2^{2+} reduction reactions, and/or expulsion of Hg in soil gas (Lindberg et al., 1999). At one site on the alluvium where a negative flux had been recorded at midday during two separate visits (140F and 158F), Hg flux measurements were initiated at 8 PM (Fig. 2). Both incident sunlight and the addition of water to the soil surface caused an immediate increase in flux from negative to positive (Fig. 2). Alluvium soils are low in Hg concentration ($19\text{--}144\text{ ng g}^{-1}$; Table 1). The change in Hg flux from negative to positive with the addition of water and incident light indicates that Hg is available for release from these soils. This same field experiment was repeated a few days after a rainstorm event and the addition of water had no effect on the Hg flux. This suggests that the alluvium soils in this area cycle between sorbing and releasing Hg as the meteorological conditions change from dark to light and dry to wet.

Twelve sampling sites were situated at the same locations, where McCarthy and McGuire (1998) measured soil gas concentrations across the north end of the Carlin Trend. All sampling locations along this transect,

with the exception of two, yielded negative Hg flux values. McCarthy and McGuire (1998) found anomalies of H_2 and CO_2 in soil gas along this transect and attributed this to gas movement along structures of the Carlin Trend. The fact that no Hg flux was measured at these sites, where anomalous readings were obtained by McCarthy and McGuire (1998), may be due to lack of Hg gas movement from the subsurface, lack of physical correlation between the gases, or the reaction of migrating Hg gases with substrate.

3.2. Laboratory Hg flux experiments

To further investigate the observed uptake and release of Hg from alluvial soils in the Ivanhoe Mining District, controlled laboratory experiments were conducted with the same alluvial soils from which Hg flux was measured in situ. Fig. 3 illustrates the response to light exhibited by alluvium sample 158F from which an in situ flux of $-4.4\text{ ng m}^{-2}\text{ h}^{-1}$ was measured. In the laboratory, Hg emissions from this substrate were $0.14 \pm 2.75\text{ ng m}^{-2}\text{ h}^{-1}$. This higher flux measured for the alluvial soils in the laboratory, as compared to those measured in the field, may be due to disturbance of the original soil structure that occurred with sample collection. Disturbance of soil has demonstrated to exacerbate Hg flux (Gustin et al., 2000a).

Upon turning on a fluorescent light ($\sim 4.0\text{ }\mu\text{mol m}^{-2}\text{ s}^{-1}$) in the room, Hg flux increased from 0.14 ± 2.75 to $10.6 \pm 5.8\text{ ng m}^{-2}\text{ h}^{-1}$ (Fig. 3) and remained as such for several hours. No change in temperature of the soil occurred with the addition of light. ANOVA analysis indicated that Hg fluxes measured before and after the addition of light were significantly different ($p < 0.05$). An increase in Hg flux with light has also been observed in other laboratory (Gustin et al., 1999b, 1997) and field experiments (McCarthy, 1972; Poissant et al., 1999).

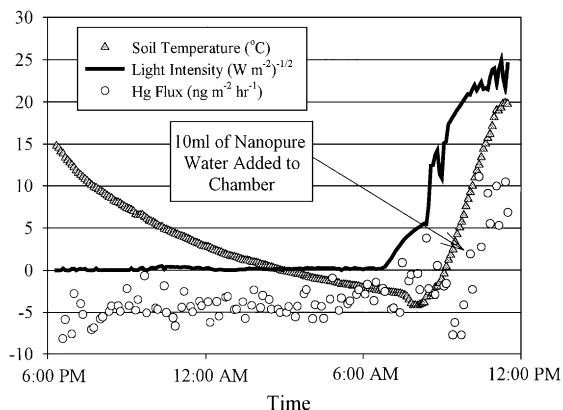


Fig. 2. Plot of soil temperature, light intensity, and Hg flux measured for alluvium in the field. Note a peak in Hg flux with first light and after the application of 10 ml of nanopure water.

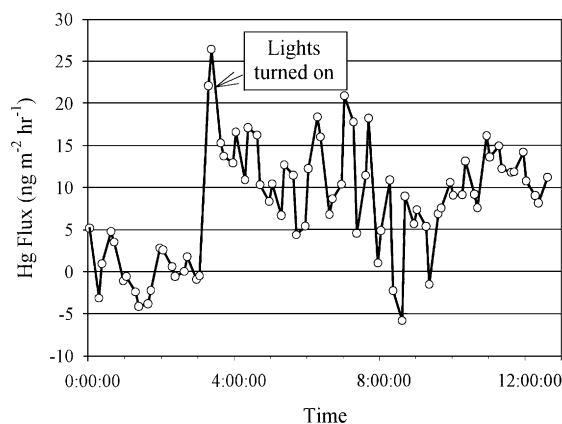


Fig. 3. Response of Hg flux measured for alluvium soil to incident light at constant temperature in a laboratory setting.

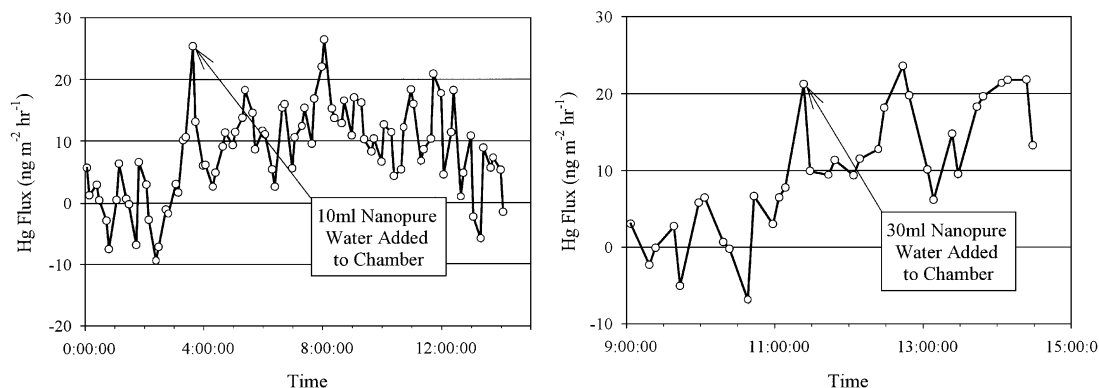


Fig. 4. (a) Response of Hg flux measured for alluvium to the application of 10 ml nanopure water in a laboratory setting. (b) Response of Hg flux measured for alluvium to the application of 30 ml nanopure water in a laboratory setting.

Aliquots of nanopure water (10 and 30 ml) were added on separate days to the same soil used in the light manipulation (Fig. 4). With the addition of water an immediate increase in flux was observed (up to 25 ng m⁻² h⁻¹) and the flux remained elevated for approximately 8 h (Fig. 4a). The same response was observed for the second addition of water (30 ml) approximately 24 h later (Fig. 4b). ANOVA results indicated that Hg fluxes measured before and after both additions of water were significantly different ($p < 0.05$). This repeatable Hg release, with the addition of nanopure water, illustrates how precipitation may facilitate Hg emissions from these desert alluvium soils. A significant increase in Hg emissions from desert soils with a precipitation event was reported as occurring during the Nevada STORMS project (Lindberg et al., 1999).

To determine if ambient air concentrations influence Hg flux to and from soils, alluvium from Ivanhoe was exposed to air containing <0.2, 20, and 220 ng Hg m⁻³ in cleaned air, and approximately 3 ng Hg m⁻³ in ambient air. No change in Hg flux was observed as air Hg concentrations were changed from ambient (3.9 ± 2.2 ng m⁻³) to ~ 0 ng m⁻³. When air with 220 ng Hg m⁻³ was introduced to the chamber, measured flux was -519 ± 34.5 ng m⁻² h⁻¹ (Fig. 5). When soils were exposed to 20 ng Hg m⁻³ air, Hg flux was -20.5 ± 6.2 ng m⁻² h⁻¹ (Fig. 6). Based on the total Hg input into the chamber and the area of soil exposed, an estimated 5–10% of the total gaseous Hg in the chamber air was sorbed by the soils. This rate of Hg uptake by soils is similar to rates seen in soils from southeastern Montana (Fang, 1978; Landa, 1978). After removal of Hg in the air stream entering the chamber, soil fluxes returned to values higher than those occurring prior to exposure suggesting desorption of some of the sorbed Hg from the soils (Figs. 5 and 6).

Incident light and amendments of water to low Hg bearing alluvium soils resulted in the release of Hg from

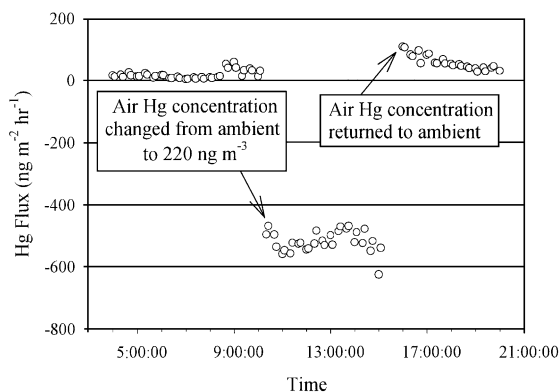


Fig. 5. Graph showing the uptake of elemental Hg by alluvium during exposure to Hg enriched air (220 ng m⁻³).

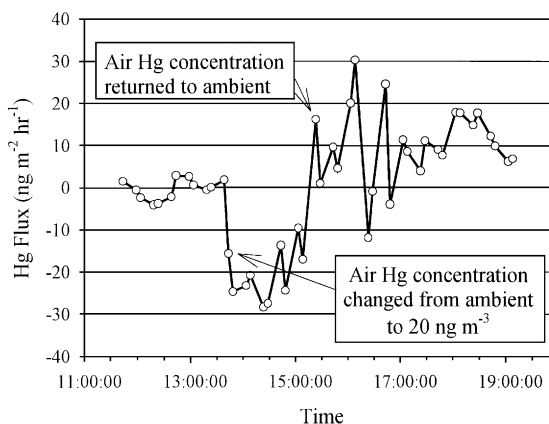


Fig. 6. Graph showing the uptake of elemental Hg by alluvium during exposure to Hg enriched air (20 ng m⁻³).

soils in situ and in a laboratory environment. Elevated Hg concentrations in air resulted in Hg uptake by alluvial soils, while air with Hg concentrations less than

ambient levels elicited no effect. These results indicate that atmospheric Hg can be sorbed and re-emitted by these soils with background Hg concentrations and that constant cycling of Hg could occur between these soils and the atmosphere.

3.3. Regression analysis of environmental variables

The relative importance of measured environmental variables on controlling Hg flux was determined using stepwise multivariate regression analysis (Table 2). Based on the F-value, the combined parameters of lithology, the natural log of soil Hg concentration, and the natural log of distance from faults were the most significant in influencing Hg flux ($p < 0.001$). These three factors accounted for 59.3% of the variance in the data. At $p < 0.01$, all variables were shown to have some effect on Hg flux which accounts for 67.0% of the variance in the data. Barometric pressure was also measured at some sights and did not correlate well with Hg flux. Previous studies have indicated log Hg soil concentration and log Hg flux are positively correlated (Gustin et al., 2000b; Rasmussen et al., 1998). This study found a good correlation ($R^2 = 0.70$) between log of the bulk soil Hg concentration and the log of measured flux.

3.4. Data normalization and district-wide flux calculation

Fig. 7 shows two diel data sets of Hg flux obtained using field flux chambers. One data set was collected slightly south of the Ivanhoe Mining District over soils containing $0.04\text{--}0.08\text{ }\mu\text{g Hg g}^{-1}$ in the $<2\text{ mm}$ grain-size fraction and $0.4\text{--}6.3\text{ }\mu\text{g Hg g}^{-1}$ in the $>2\text{ mm}$ grain-size fraction. The other diel data set was collected at the McLaughlin Gold Mine, CA, where the substrate Hg concentration in the $<2\text{ mm}$ grains-size fraction was $213\text{ }\mu\text{g Hg g}^{-1}$. The Ivanhoe Mining District diel measurement was measured using the ORNL Teflon[®] flux

chamber and the McLaughlin Gold Mine diel measurement was obtained using the UNR polycarbonate flux chamber method. The Hg enrichment at the Ivanhoe and McLaughlin Mining Districts are similar in age and origin, with respect to the type of hydrothermal system. The fluxes at McLaughlin ($117\text{--}12,214\text{ ng m}^{-2}\text{ h}^{-1}$) were ~ 250 times higher than those measured at Ivanhoe (-8.40 to $50.9\text{ ng m}^{-2}\text{ h}^{-1}$) due primarily to higher substrate Hg concentrations. If the diel flux data from Ivanhoe are multiplied by 250, a pattern of Hg flux is obtained that is similar to the McLaughlin diel flux (Fig. 7). These two data sets illustrate the fact that Hg measurements taken during one time of the day may be quite different from measurements taken during other times of the day. This leads to difficulty in comparing measurements from independent sites at different times and in using flux measurements collected at one time of day for scaling up Hg emissions. The two diel data sets

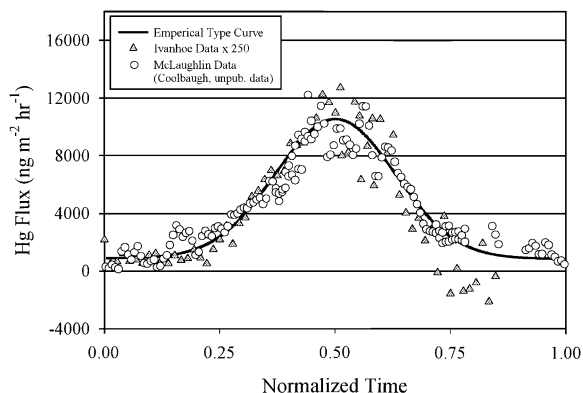


Fig. 7. Diel Hg flux measurements from Ivanhoe, NV and McLaughlin, CA. Solid black line is Gaussian curve best-fit to the data. Despite more than two orders of magnitude difference between the data sets, the shape of the curves are identical.

Table 2

Results from stepwise multivariate regression analysis assessing the hierarchy of environmental variables controlling Hg flux. Parameters are ranked from greatest to least importance

Variable	Multiple		% Increase in R^2	F-value
	R	R^2		
Lithology	0.535	0.286		9.23 ^a
ln of Hg soil concentration	0.656	0.430	50.3	8.30 ^a
ln of distance from faults	0.770	0.593	37.9	10.19 ^{a,b}
Light intensity	0.791	0.626	5.56	8.38 ^a
Soil temperature outside chamber	0.812	0.660	5.43	7.36 ^a
Soil temperature inside chamber	0.815	0.664	0.61	5.94 ^a
Air temperature	0.817	0.667	0.45	4.87 ^a
Relative humidity	0.819	0.670	0.46	4.06 ^a

^aSignificant at 0.01 level.

^bSignificant at 0.001 level.

follow a Gaussian distribution (Fig. 7) that is described using the following empirically derived equation:

$$F = C_1 \left[\frac{1}{\sqrt{0.26\pi}} e^{-(t-1/2)^2/(2 \times 0.13^2)} \right],$$

where F is the Hg flux in $\text{ng m}^{-2} \text{h}^{-1}$, C_1 a coefficient of flux, the magnitude of which is specific to each sample location and day, and t the time of day normalized from 0 to 1 (e.g. 12:00 PM = 0.5). Using this equation to calculate the average flux for a location, the time of day and measured Hg flux are entered into the equation to find the coefficient C_1 . Then Hg flux is calculated for the day on 5 min intervals, which are summed, producing a total 24-hour flux. This total flux is divided by 24 h to get the average hourly flux ($\text{ng m}^{-2} \text{h}^{-1}$) for the site for the day of sampling. This technique provides a means of calculating area average flux for an area using single measurements.

Net Hg deposition was observed during the diel measurement at Ivanhoe, in the evening (Fig. 7). The Gaussian distribution equation does not account for deposition. However, the amount of Hg that is deposited is quite small relative to the amount of Hg emitted during the rest of the day. Therefore, the period of net deposition is considered negligible and is ignored in the Gaussian model.

To scale up emissions for the study area (Fig. 1), lithology was used as the predominant variable controlling flux (Table 2). A net flux of $0 \text{ ng m}^{-2} \text{h}^{-1}$ was applied to alluvium based on the observation that deposition and reemission could occur from these soils. The metamorphic rocks comprise a fairly small area ($\sim 5.6 \text{ km}^2$) and contain little Hg relative to the overlying rocks (Bailey and Phoenix, 1944), and therefore were not included in the area flux estimate. For the area covered by mafic and felsic volcanic rocks, the flux applied represents the mean of the average hourly fluxes calculated for each flux measurement site in that unit, 14.9 and $21.6 \text{ ng m}^{-2} \text{h}^{-1}$ respectively. Using these values and the area of lithologic units, determined with GIS, the calculated flux for the 586 km^2 area was $7.8 \times 10^4 \pm 5.9 \times 10^4 \text{ g yr}^{-1}$. This results in an average emission rate of $15.2 \pm 11.5 \text{ ng m}^{-2} \text{h}^{-1}$, for the entire area. It is expected, given the dependence of Hg emission on temperature (Gustin et al., 1997), that higher Hg emissions will occur in the summer and lower emissions in the winter. Since the flux data presented in this study were collected in the fall, when meteorological conditions are representative of average yearly conditions, they are considered representative of average yearly values.

The above flux estimate does not take into account emissions from mine wastes and ore zones within the district. The average hourly flux calculated for the mined open pit of the Silver Cloud mine was $27,600 \text{ ng m}^{-2} \text{h}^{-1}$ (104F) while tailings and mine waste in the area had

an average hourly flux of $226 \text{ ng m}^{-2} \text{h}^{-1}$ (102F). The pit covers $\sim 18,000 \text{ m}^2$; assuming that Hg flux was homogeneous from the surface area of the open pit, the total flux from the pit would be $4.35 \times 10^3 \text{ g yr}^{-1}$. Using an area of $26,000 \text{ m}^2$ for the tailings near the Silver Cloud mine, the calculated flux from the tailings is 52 g yr^{-1} . Hence, the total flux from the disturbed area of the Silver Cloud mine is roughly $4.4 \times 10^3 \text{ g yr}^{-1}$. The Butte Quicksilver mine produced roughly the same amount of Hg as the Silver Cloud mine (Bailey and Phoenix, 1944). Assuming the degree of mineralization is also similar, it is expected that another $4.4 \times 10^3 \text{ g yr}^{-1}$ is released from the Butte Quicksilver mine. Emissions measured from mine waste, which covers a $\sim 5500 \text{ m}^2$ area at Governor mine, were $280 \text{ ng m}^{-2} \text{h}^{-1}$, resulting in an annual emission of 13.5 g yr^{-1} of Hg. Three other mines within the district produced roughly the same amount of Hg as the Governor mine, the Fox mine, the Lark prospects, and the Rimrock mine (Bailey and Phoenix, 1944). Given the similar size of these mines it is expected that an additional 54 g yr^{-1} is emitted from these four mines. This is a conservative estimate because the flux measurements made on mine sites and mine waste were made using a low field chamber turnover rate. The total sum of Hg released from anthropogenically disturbed areas in the district is $8.9 \times 10^3 \text{ g yr}^{-1}$.

The total yield from point sources (mines and mine waste) and non-point sources (rocks that are slightly enriched in Hg throughout the district) is $8.7 \times 10^4 \text{ g yr}^{-1}$ of Hg. Non-point sources are the largest contributor ($\approx 89\%$) to total Hg emissions. The area averaged flux for the entire Ivanhoe Mining District including ore zones and tailings is $17.1 \text{ ng m}^{-2} \text{h}^{-1}$. Navarro-Flores et al. (2000) estimated an area averaged Hg emission factor of $33.8 \text{ ng m}^{-2} \text{h}^{-1}$ for the Valle del Azogue deposit in Spain and an annual emission of $29.2 \text{ g Hg yr}^{-1}$ from the 0.098 km^2 area. This deposit is geologically similar to the Ivanhoe deposits. The fact that through two independent methods relatively similar emission rates are predicted for these areas suggests that these flux estimates are not unreasonable.

4. Conclusions

Desert alluvium with low Hg concentrations can act as sites of Hg emission and deposition. Field and lab experiments demonstrated that elevated concentrations of Hg in air resulted in Hg deposition while incident light and precipitation triggered Hg release. This suggests that short-term cycles of Hg uptake and release may result in a net flux of zero associated with these substrates and other substrates with low Hg concentration and that Hg cycling between the atmosphere and substrate may occur on a daily time step.

Previous studies have shown that Hg soil concentrations can be used to estimate Hg flux with a high degree of certainty (Gustin et al., 2000b; Rasmussen et al., 1998). In this study area, lithology, Hg soil concentration, and distance from the nearest fault were found to be the most important factors in controlling Hg flux. These features of any mineralized area may be used to aid in the estimation of natural Hg emissions.

The Ivanhoe Mining District contributes $\sim 8.7 \times 10^4$ g of Hg annually to the atmosphere. This flux is roughly equivalent to the annual Hg emission from a 700 MW coal-fired power plant (Chu and Porcella, 1995). In this district, the bulk of the Hg released into the atmosphere ($\approx 89\%$) is from non-point sources (that is large areas of natural enrichment where no mining or any other major human disturbance has occurred), while 11% is emitted from areas of mining and anthropogenic disturbance. The average flux from the district, $17.1 \text{ ng m}^{-2} \text{ h}^{-1}$, exceeds the natural emission factor applied to Hg rich belts of the world ($1.5 \text{ ng m}^{-2} \text{ h}^{-1}$) in global models (Lindqvist et al., 1991; Mason et al., 1994) by more than an order of magnitude. The uncertainty associated with this emission estimate is on the order of 50–75% based on the standard deviation for the flux averages for undisturbed lithologic units. The standard deviation represents spatial variability in Hg flux within specific lithologic units across a large area. Results from this study suggest that the natural contribution of Hg to the atmosphere may be underestimated. In order to fully assess the contribution of Hg to the atmosphere from natural sources, emissions from a variety of geologic terranes must be measured and scaled to provide regional Hg emission estimates.

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